

STATUTORY DECLARATION

I, Jun Hee PARK, a citizen of the Republic of Korea and a staff member of Bae, Kim & Lee, specializing in "Semiconductor Devices", do hereby declare that:

1) I am conversant with the English and Korean languages and am a competent translator thereof;

2) To the best of my knowledge and belief, the following is a true and correct translation of the Priority Document (No. KR 2000-34103) in the Korean language already filed with the Korean Intellectual Property Office on June 21, 2000.

Signed this February 12, 2003

*Jun Hee Park*

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Jun Hee PARK



THE KOREAN INTELLECTUAL PROPERTY OFFICE

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Application No.: Patent Application No. 2000-34103

Date of Application: June 21, 2000

Applicant: Hynix Semiconductor Inc.

June 5, 2001

COMMISSIONER

# PHOTORESIST POLYMER FOR TOP SURFACE IMAGING PROCESS AND PHOTORESIST COMPOSITION CONTAINING THE SAME

## BACKGROUND OF THE INVENTION

### 5 Field of the Invention

The present invention relates to a photoresist polymer for a top-surface  
imaging process, and a photoresist composition containing the same. In particular,  
the present invention relates to a polymer of Formula 1 which can perform a silylation  
process by selectively abscission of protecting group in an exposed region to generate  
10 a hydroxyl group, and by reacting the hydroxyl group with a silylation agent, and a  
photoresist composition containing the same.

### Description of the Background Art

A photoresist requires a low absorbency at an independent wavelength, an  
15 excellent etching resistance and adhesiveness to the wafer, and has to be developed in  
2.38 wt% and 2.6 wt% aqueous tetramethylammonium hydroxide (TMAH) solution  
in order to be employed a photoresist layer for ArF, VUV, EUV and E-beam.

There has been much research done on resins having a high transparency at a  
wavelength of 193 nm and etching resistance similar to Novolak resin. However,  
20 most of the resists are not suitable for VUV due to their strong absorbency at 157 nm  
wavelength. In order to supplement the above problem, there has been intensive  
research done on resins containing fluorine and silicon. However they have the  
defects such as the following independently. Photoresists containing fluorine with a  
polyethylene or polyacrylate polymer backbone have weak etching resistance, low  
25 solubility in an aqueous TMAH solution and poor adhesiveness to the silicon wafer.  
In addition, these photoresists are difficult to mass-produce and are expensive.

Furthermore, during a post-exposure bake (PEB) process these photoresist can generate HF which can contaminate a lens or corrode a device. Thus, these photoresists are generally not suitable for commercial use. On the other hand, photoresists containing silicon satisfy required silicon content (over 10%) in the etching step. For this, monomers comprising silicon are used in large volume, which increases hydrophobicity of the photoresists. Therefore, the photoresist cannot satisfy selectivity between an exposed region and a non-exposed region in aqueous TMAH solution, and has low adhesiveness to the silicon wafer.

Some of the known problems of the photolithography include substrate's influence on the light, notching, standing wave effect, pattern collapse, non-uniformity of a critical dimension (CD), isolated and grouped bias (IG bias) and the like. Top surface imaging process is researched for a solution of the above problems. In TIPS, a shallow exposure is performed which forms a latent image by diffusion of acids that is generated in the exposed region. The exposed region is then selectively silylated with a silylating agent. The silylated region serves as a mask, and the non-silylated region is dry-etched by O<sub>2</sub> plasma. Thus, TIPS requires photoresist compositions having a high energy absorption coefficient and process conditions that have high selectivity in etching non-silylated regions during O<sub>2</sub> plasma treatment.

This TIPS is single layer resist process, if using the TIPS, we can eliminate standing wave effect, multiplex interference effect and notching, and increase a resolution and depth of focus.

Accordingly, the present inventors have studied to prepare a photoresist polymer suitable for using TIPS and completed this invention by developing the polymer of Formula 1 which can be selectively silylated by generating hydroxyl group after light exposure. The problem of prior art can be overcome if performing TIPS using this polymer.

## SUMMARY OF THE INVENTION

An Object of this present is to provide a photoresist (PR) polymer and a photoresist composition containing the same for TIPS using a light source such as KrF, ArF, VUV (157nm), EUV (13nm) and E-beam.

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## BRIEF DESCRIPTION OF THE DRAWINGS

Figure 1 is a schematic view illustrating TIPS in accordance with the present invention;

Figure 2 shows a pattern obtained in Example 3;

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Figure 3 shows a pattern obtained in Example 4; and

Figure 4 shows a pattern obtained in Example 5.

## DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

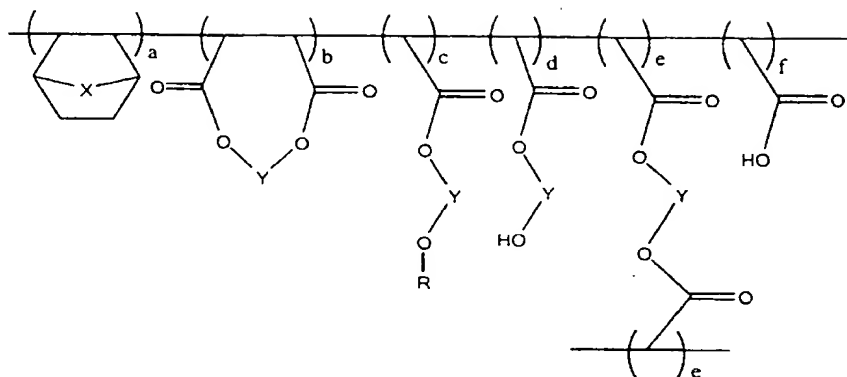
To achieve the above objectives the present invention provides a novel  
15 polymer of Formula 1 which is capable of generating hydroxyl group selectively by light exposure; a photoresist composition containing the above polymer; and process for forming of photoresist pattern using the above photoresist compositions.

The present invention will be described in detail hereinafter.

Firstly, the present invention provides a photoresist polymer represented by  
20 following Formula 1.

25

[Formula 1]



wherein, X is CH<sub>2</sub>, CH<sub>2</sub>CH<sub>2</sub>, O or S,

Y is linear or branched (C<sub>1</sub>-C<sub>10</sub>) alkyl group, or ether group,

5 R is an acid labile protecting group such as tert-butyl, tetrahydropyranyl, methyl tetrahydropyranyl, tetrahydrofuranyl, methyl tetrahydrofuranyl, methoxyethyl, 2-methoxypropyl, ethoxyethyl, 2-ethoxypropyl, tert-butoxyethyl, acetoxyethoxyethyl, acetoxymenthyl, tert-butoxycarbonyl and isobutoxyethyl, and

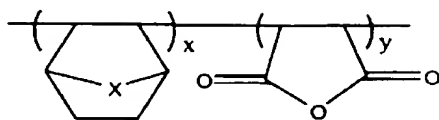
10 a : b : c : d : e : f is 20-40mol% : 0-20mol% : 20-70mol% : 0-30mol% : 0-20mol% : 0-20mol%.

In the compound of Formula 1, it is preferable that X is CH<sub>2</sub>, Y is CH<sub>2</sub>CH<sub>2</sub> or CH<sub>2</sub>CH<sub>2</sub>OCH<sub>2</sub>CH<sub>2</sub>, and R is tert-butyl.

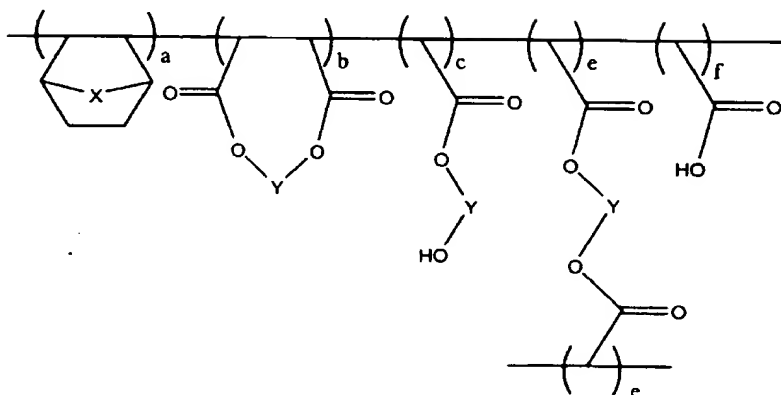
The polymer of Formula 1 can be prepared by the process comprising the steps of:

- 15 (a) polymerizing alicyclic monomer with maleic anhydride to obtain a polymer of following Formula 2;
- (b) reacting the polymer of Formula 2 with diol compound of following Formula 4 to obtain a polymer of following Formula 3; and
- (c) reacting the polymer of Formula 3 with a compound having an acid
- 20 labile protecting group to obtain a polymer of Formula 1 where a hydroxyl group is partially protected.

[Formula 2]



[Formula 3]



5

[Formula 4]

HO-Y-OH

wherein, X is CH<sub>2</sub>, CH<sub>2</sub>CH<sub>2</sub>, O or S;

Y is linear or branched (C<sub>1</sub>-C<sub>10</sub>) alkyl group or ether group;

R is an acid labile protecting group including tert-butyl, tetrahydropyranyl,

10 methyl tetrahydropyranyl, tetrahydrofuranyl, methyl tetrahydrofuranyl, methoxyethyl, 2-methoxypropyl, ethoxyethyl, 2-ethoxypropyl, tert-butoxyethyl, acetoxyethoxyethyl, acetoxymethyl, tert-butoxycarbonyl and isobutoxyethyl,

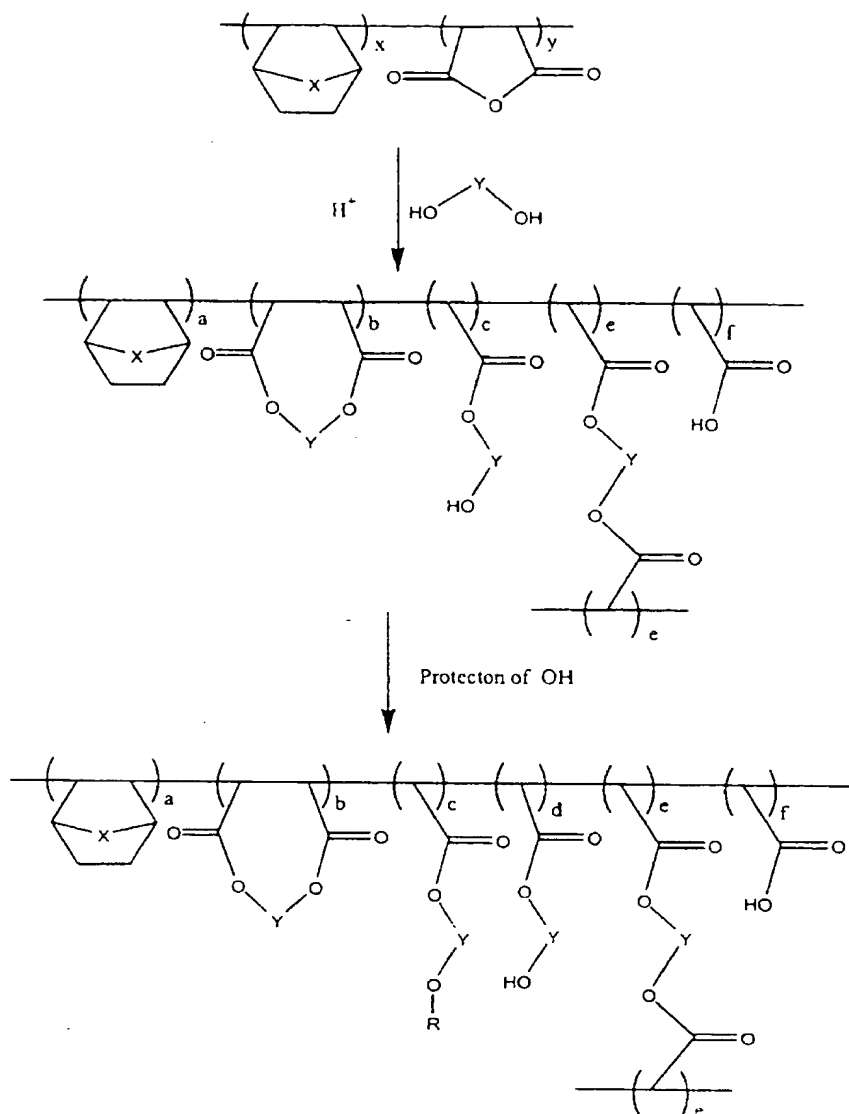
in Formula 2, x : y is 20-40mol% : 60-80mol%; and

in Formula 3, a : b : c : e : f is 20-40mol% : 0-20mol% : 20-80mol% : 0-

15 20mol% : 0-20mol%.

The preparation process for the polymer of Formula 1 is represented in following Reaction Scheme 1.

[Reaction Scheme 1]



In the above preparing process, the compound having the protecting group preferably comprises the compound having the group of tert-butylcarboxylate, ( $C_1$ - $C_{20}$ ) alkyl, ( $C_1$ - $C_{20}$ ) aryl or ( $C_1$ - $C_{20}$ ) arylvinylether; and the protecting group is preferably selected from the group consisting of tert-butyl, tetrahydropyranyl, methyl tetrahydropyranyl, tetrahydrofuranyl, methyl tetrahydrofuranyl, methoxyethyl, 2-methoxypropyl, ethoxyethyl, 2-ethoxypropyl, tert-butoxyethyl, acetoxyethoxyethyl, acetoxymethyl, tert-butoxycarbonyl and isobutoxyethyl.



In above polymerization process, polymerization solvent is selected from the group consisting of tetrahydrofuran, dimethylformamide, dimethylsulfoxide, dioxane, benzene, toluene and xylene.

5 In addition, the above preparation process further comprises the step which is crystallizing and purifying the polymer prepared in step (c). The solvent for crystallization and purification of the polymer is preferably selected from the group consisting of hexane; diethyl ether; petroleum ether; lower alcohol such as methanol, ethanol and isopropanol; water; and mixture thereof.

10 Another aspect is to provide a polymer of Formula 3 which is used as an intermediate for preparing the photoresist polymer of Formula 1.

In addition, the present invention provides a photoresist composition comprising (i) the photoresist polymer of Formula 1, (ii) a photoacid generator; and (iii) an organic solvent.

15 The photoacid generator is preferably selected from the group consisting of phthalimidotrifluoromethane sulfonate, dinitrobenzyltosylate, n-decyl disulfone and naphthylimido trifluoromethane sulfonate which have a relatively low light absorbency in the wavelengths of 157 nm and 193 nm.

20 The photoacid generator can further comprise a sulfide or onium type compound selected from the group consisting of diphenyl iodide hexafluorophosphate, diphenyl iodide hexafluoroarsenate, diphenyl iodide hexafluoroantimonate, diphenyl p-methoxyphenyl triflate, diphenyl p-toluenyl triflate, diphenyl p-isobutylphenyl triflate, triphenylsulfonium hexafluoroarsenate, triphenylsulfonium hexafluoroantimonate, triphenylsulfonium triflate and dibutylnaphthylsulfonium triflate.

25 The photoacid generator is used in an amount of 0.1 to 10wt% of the photoresist resin employed.

In addition, organic solvent used in the photoresist composition is selected from the group consisting of ethyl 3-ethoxypropionate, methyl 3-methoxypropionate, cyclohexanone, propyleneglycol methyletheracetate, n-heptanone and ethyl lactate.

The amount of solvent used is preferably in the range of from about 300 % to  
5 about 1500% by weight of the photoresist polymer. This ratio has been found to be particularly useful in obtaining a photoresist layer of a desirable thickness when coated on to a suitable substrate such as a silicon wafer in production of a semiconductor element. In particular, it has been found by the present inventors that when the amount of organic solvent is about 800% by weight of the photoresist  
10 polymer, a photoresist composition layer having 0.3  $\mu\text{m}$  of thickness can be obtained.

Yet another aspect provides a process for forming a photoresist pattern, comprising the steps of:

- (a) coating a photoresist composition on a substrate of a semiconductor element to form a photoresist film;
- 15 (b) exposing the photoresist film;
- (c) performing silylation process on the surface of the exposed photoresist film; and
- (d) dry etching the photoresist film using the silylated layer as an etching mask to obtain a negative pattern.

20 The process further includes the step of pre-treating the substrate with hexamethyldisilazane (HMDS) before step (a). This is the process which causes the chemical reaction between  $\text{Si}(\text{CH}_3)_3$  of HMDS  $[(\text{CH}_3)_3\text{Si}-\text{NH}-\text{Si}(\text{CH}_3)_3]$  and hydroxyl group present in the surface of the substrate, thus improves adhesiveness between the substrate and the photoresist composition by making the surface of the substrate  
25 hydrophobic.

Soft baking step before exposure transforms the photoresist composition into a

solid-type resist film by evaporating the organic solvent in the photoresist composition with heat energy.

In the exposure step, a light penetrating through the exposure mask selectively generates a photochemical reaction of the photoresist merely in the exposed region, thus maintaining overlay accuracy with a previously-formed pattern.

A pre-silylation baking (PSB) step is performed after the exposure. The pre-silylation baking step causes a difference in solubility due to a chemical reaction which takes place between the photoresist resin and acids ( $H^+$ ) generated by exposure. That is, the protecting group of the photoresist polymer is deprotected in the PSB step, and thus the hydroxyl group is selectively generated in the exposed section. Accordingly, the silylation is mainly performed in the exposed region, and thus a negative pattern is formed after dry-etching.

The above soft baking process and PSB process is performed at temperature ranging from 10 to 200°C.

And the above exposing process is performed with irradiation energy ranging from 1 to 50mJ/cm<sup>2</sup> using ArF, KrF, EUV (Extreme Ultra Violet), VUV (Vacuum Ultra Violet), E-beam, X-ray and ion beam.

The silylating agent for the silylation process is preferably selected from the group consisting of hexamethyldisilazane, tetramethyldisilazane, bisdimethyl amino dimethyl silane, bisdimethyl amino methyl silane, dimethylsilyl dimethylamine, dimethylsilyl diethylamine, trimethylsilyl dimethylamine, trimethylsilyl diethylamine and dimethylamino pentamethyldisilane. The silylation agent can be employed in a vapor or in a liquid phase.

In the silylation process, it is believed that the silylating agent diffuses and penetrates into the photoresist resin. The hydroxyl group present in the photoresist resin reacts with the silylating agent to form dangling bond. When thermal energy

or moisture ( $H_2O$ ) is added, the silylating agent diffuses out easily. Therefore the silylation and dry development processes are preferably performed in a single chamber connected with cluster.

On the other hand, the present photoresist composition is not always employed in TIPS, it can be employed to form a general pattern.

In another embodiment, the present invention also provides a semiconductor element that is manufactured using the photoresist composition described above.

The present invention will now be described in more detail by referring to the examples below, which are not intended to be limiting.

#### 10 I. Preparation of Photoresist Polymer

##### Example 1

##### (Step 1) Synthesis of Poly(norbornene/maleic anhydride)

To 50ml of tetrahydrofuran was added 0.2 mole of norbornylene, 0.2 mole of maleic anhydride and 0.4g of AIBN. The resulting mixture was reacted at 67°C for 15 24 hours. Thereafter, the polymer was precipitated and filtered in petroleum ether/ether (1/1) solution, to obtain poly(norbornene/maleic anhydride) of Formula 2 wherein X is  $CH_2$  (yield : 65%).

##### (Step 2) Synthesis of Poly(norbornene/dihydroxyethylfumalate)

To 300ml of anhydrous ethylene glycol ( $HO-CH_2CH_2-OH$ ) was added 19.2g of 20 poly(norbornene/maleic anhydride) prepared in step 1, and 0.1ml of sulfuric acid. The resulting mixture was reacted at 150°C for 10 hours. After cooling the resulting solution, 100ml of water was added thereto. Thereafter, the esterized polymer was precipitated, filtered and dried, to obtain poly(norbornene/dihydroxyethylfumalate) of Formula 3 wherein X is  $CH_2$ , and Y is  $CH_2CH_2$  (yield : 96%).

##### 25 (Step 3) Protection of Hydroxyl Group

To 50ml of dimethylformamide was added 10g of compound prepared in

Step 2, and 20g of di-tert-butyl dicarbonate, and the resulting mixture was reacted at a room temperature for 12 hours. Thereafter, the polymer was precipitated and purified in hexane, to obtain the polymer of Formula 1 wherein X is CH<sub>2</sub>, Y is CH<sub>2</sub>CH<sub>2</sub>, and R is tert-butyl (yield : 97%).

5            Example 2

(Step 1) Synthesis of Poly(norbornene/dihydroxyethoxyethylfumalate)

To 300ml of anhydrous diethylene glycol (HO-CH<sub>2</sub>CH<sub>2</sub>OCH<sub>2</sub>CH<sub>2</sub>-OH) was added 19.2g of poly(norbornene/maleic anhydride) prepared in Step 1 of Example 1, and 0.1ml of sulfuric acid, and the resulting solution was reacted at 150°C for 10  
10 hours. Thereafter, the resulting solution was cooled, and 100ml of water was added thereto. The esterized polymer was precipitated, filtered and dried, to obtain poly(norbornene/dihydroxyethoxyethylfumalate) of Formula 3 wherein X is CH<sub>2</sub>, and Y is CH<sub>2</sub>CH<sub>2</sub>OCH<sub>2</sub>CH<sub>2</sub> (yield : 94%).

(Step 2) Protection of Hydroxyl Group

15 To 50ml of dimethylformamide was added 10g of compound prepared in step 1 of Example 2, and 20g of di-tert-butyl dicarbonate, and the resulting solution was reacted at a room temperature for 12 hours. Thereafter, the polymer was precipitated and purified in hexane, to obtain the polymer of Formula 1 wherein X is CH<sub>2</sub>, Y is CH<sub>2</sub>CH<sub>2</sub>OCH<sub>2</sub>CH<sub>2</sub>, and R is tert-butyl (yield : 97%).

20 II.        Preparation of Photoresist Compositions and Formation of Patterns

Example 3

To 100g of propyleneglycol methyl ether acetate was added the polymer prepared in Example 1 (10g), phthalimidotrifluoromethane sulfonate (0.06g) and triphenylsulfonium triflate (0.06g). The resulting mixture was stirred and filtered  
25 through 0.20μm filter to obtain a photoresist composition.

The photoresist composition was coated on a silicon wafer to form a

photoresist thin film. The thin film was soft-baked in an oven or hot plate at 130°C for 90 seconds, exposed to light using an ArF exposer, post-baked at 130°C for 90 seconds, and developed in the 2.38wt% aqueous TMAH solution to obtain 110nm L/S pattern (see Figure 2).

5            Example 4

To propyleneglycol methyl ethyl acetate (100g) was added the polymer prepared in Example 1(10g), phthalimidotrifluoromethane sulfonate (0.06g) and triphenylsulfonium triflate (0.06g). The resulting solution was filtered through 0.20μm filter to obtain a photoresist composition.

10           In order to evaluate the L/S pattern by the TIPS, the photoresist composition was spin-coated on a bare silicon wafer at a thickness of about 3000Å, and soft-baked at 100°C for 60 seconds. After baking, the photoresist was exposed to light by using ISI ArF stepper (NA=0.6, Off-axis). Thereafter, the silylation was performed thereon at 100°C for 210 seconds by using gas-phase tetramethyldisilazane. On the  
15           other hand, the dry development included breakthrough for removing silicon dioxide layer in the exposed region; oxygen plasma etching and over-etching for etching a resist. The dry development was performed under the conditions of 35 sccmO<sub>2</sub>, 500W of top power, 100W of bottom power, 75W of bias, -30°C and 5mtorr. After the dry development, 110nm L/S pattern was obtained (see Figure 3).

20           Example 5

To propyleneglycol methyl ethyl acetate (100g) was added the polymer prepared in Example 2 (10g), phthalimidotrifluoromethane sulfonate (0.06g) and triphenylsulfonium triflate (0.06g). The resulting solution was filtered through 0.20μm filter to obtain a photoresist composition.

25           The procedure of Example 4 was repeated on the thusly-prepared photoresist composition, to obtain a 110nm L/S pattern (see Figure 4).

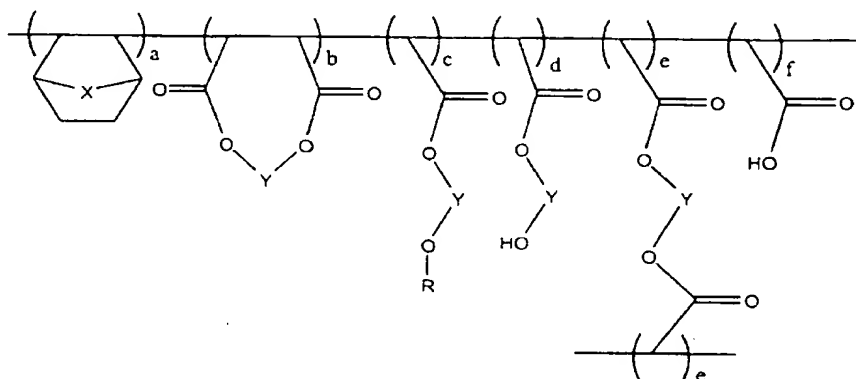
As discussed earlier, the photoresist composition can be used for the TIPS employing KrF, ArF, VUV (157nm), EUV (13nm) or E-beam as a light source.

Moreover, the photoresist composition has excellent resolution and adhesiveness, and thus can prevent a pattern collapse in forming a minute pattern.

What is claimed is:

1. A photoresist polymer represented by the following Formula 1:

[Formula 1]



5 wherein, X is CH<sub>2</sub>, CH<sub>2</sub>CH<sub>2</sub>, O or S,

Y is linear or branched (C<sub>1</sub>-C<sub>10</sub>) alkyl group or ether group,

R is an acid labile protecting group, and

a : b : c : d : e : f is 20-40mol% : 0-20mol% : 20-70mol% : 0-30mol% : 0-20mol% : 0-20mol%.

10

2. The photoresist polymer according to claim 1, wherein the acid labile protecting group is selected from the group consisting of tert-butyl, tetrahydropyranyl, methyl tetrahydropyranyl, tetrahydrofuranyl, methyl tetrahydrofuranyl, methoxy ethyl, 2-methoxypropyl, ethoxyethyl, 2-ethoxypropyl, tert-butoxyethyl, acetoxymethoxyethyl, acetoxymethyl, tert-butoxycarbonyl and isobutoxyethyl.

15

3. The photoresist polymer according to claim 1, wherein X is CH<sub>2</sub>, Y is CH<sub>2</sub>CH<sub>2</sub> or CH<sub>2</sub>CH<sub>2</sub>OCH<sub>2</sub>CH<sub>2</sub>, and R is tert-butyl.

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4. A process for preparing a photoresist polymer represented by the following Formula 1 comprising:

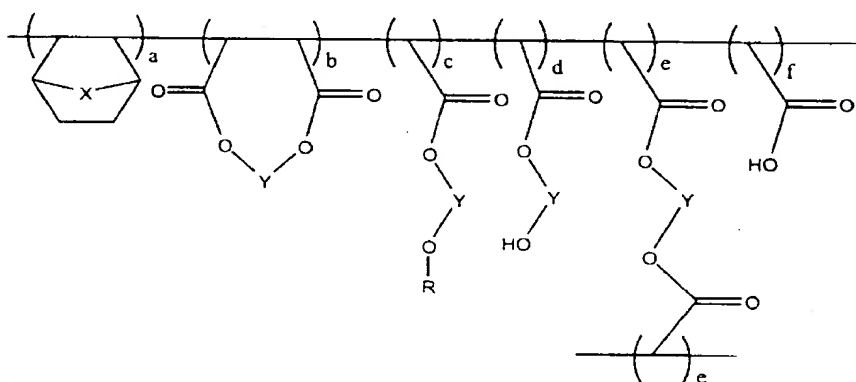


(a) polymerizing alicyclic monomer with maleic anhydride to obtain a polymer of Formula 2;

(b) reacting the polymer of Formula 2 with a diol compound of Formula 4 to obtain a polymer of Formula 3; and

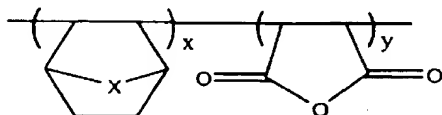
5 (c) reacting the polymer of Formula 3 with a compound having an acid labile protecting group to obtain a polymer of Formula 1 where a hydroxyl group is partially protected.

[Formula 1]

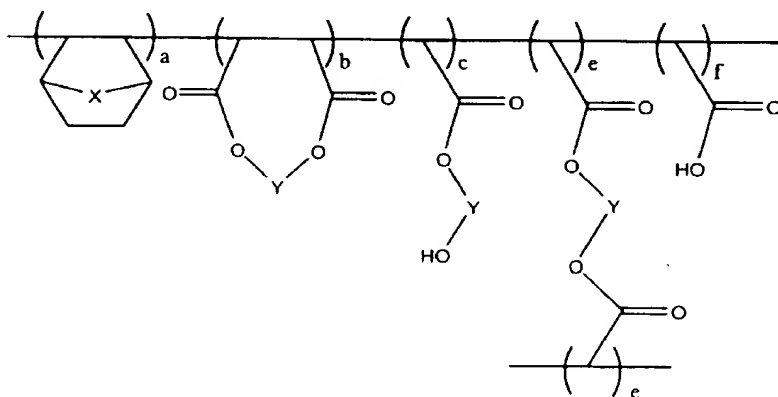


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[Formula 2]



[Formula 3]



[Formula 4]

OH-Y-OH

wherein, X is CH<sub>2</sub>, CH<sub>2</sub>CH<sub>2</sub>, O or S,

Y is linear or branched (C<sub>1</sub>-C<sub>10</sub>) alkyl group or ether group,

5 R is an acid labile protecting group,

in Formula 1, a : b : c : d : e : f is 20-40mol% : 0-20mol% : 20-70mol% : 0-30mol% : 0-20mol% : 0-20mol%;

in Formula 2, x : y is 20-40mol% : 60-80mol%; and

10 in Formula 3, a : b : c : e : f is 20-40mol% : 0-20mol% : 20-80mol% : 0-20mol% : 0-20mol%.

5. The process according to claim 4, wherein the compound having an acid labile protecting group is the compound having tert-butylcarboxylate, (C<sub>1</sub>-C<sub>20</sub>) alkyl, (C<sub>1</sub>-C<sub>20</sub>) aryl or (C<sub>1</sub>-C<sub>20</sub>) arylvinylether group.

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6. The process according to claim 5, wherein the acid labile protecting group is selected from the group consisting of tert-butyl, tetrahydropyranyl, methyl tetrahydropyranyl, tetrahydrofuranyl, methyl tetrahydrofuranyl, methoxy ethyl, 2-methoxypropyl, ethoxyethyl, 2-ethoxypropyl, tert-butoxyethyl, acetoxymethoxyethyl, 20 acetoxymethyl, tert-butoxycarbonyl and isobutoxyethyl.

7. The process according to claim 4, wherein the polymerization solvent is selected from the group consisting of tetrahydrofuran, dimethylformamide, dimethylsulfoxide, dioxane, benzene, toluene and xylene.

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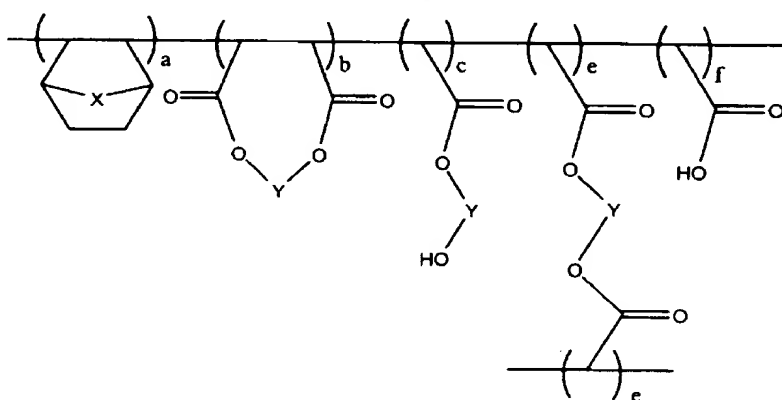
8. The process according to claim 4, wherein the process further

comprises the step which is crystallizing and purifying the polymer prepared in step (c).

9. The process according to claim 8, wherein the solvent for  
5 crystallization and purification is selected from the group consisting of hexane; diethyl ether; petroleum ether; lower alcohol comprising methanol, ethanol and isopropanol; water; and mixture thereof.

10. A polymer of following Formula 3 which is used for preparing the  
10 photoresist polymer of Formula 1.

[Formula 3]



wherein, X is CH<sub>2</sub>, CH<sub>2</sub>CH<sub>2</sub>, O or S,

Y is linear or branched (C<sub>1</sub>-C<sub>10</sub>) alkyl group or ether group,

15 R is an acid labile protecting group, and

a : b : c : e : f is 20-40mol% : 0-20mol% : 20-80mol% : 0-20mol% : 0-  
20mol%.

11. A photoresist composition comprising (i) the photoresist polymer of  
20 claim 1, (ii) a photoacid generator, and (iii) an organic solvent.

12. The photoresist composition according to claim 11, wherein the photoacid generator is selected from the group consisting of phthalimidotrifluoromethane sulfonate, dinitrobenzyltosylate, n-decyl disulfone and naphthylimido trifluoromethane sulfonate.

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13. The photoresist composition according to claim 12, wherein the photoacid generator further comprises a compound selected from the group consisting of diphenyl iodide hexafluorophosphate, diphenyl iodide hexafluoroarsenate, diphenyl iodide hexafluoroantimonate, diphenyl p-methoxyphenyl triflate, diphenyl p-toluenyl triflate, diphenyl p-isobutylphenyl triflate, diphenyl p-tert-butylphenyl triflate, triphenylsulfonium hexafluorophosphate, triphenylsulfonium hexafluoroarsenate, triphenylsulfonium hexafluoroantimonate, triphenylsulfonium triflate and dibutyl-naphthylsulfonium triflate.

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15

14. The photoresist composition according to claim 11, wherein the photoacid generator is present in an amount ranging from 0.1 to 10% by weight of the photoresist polymer.

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15. The photoresist composition according to claim 11, wherein the organic solvent is selected from the group consisting of ethyl 3-ethoxypropionate, methyl 3-methoxypropionate, cyclohexanone, propyleneglycol methyletheracetate, n-heptanone and ethyl lactate.

25

16. The photoresist composition according to claim 11, wherein the organic solvent is present in an amount ranging from 300% to 1500% by weight of the photoresist polymer.

17. A process for forming a photoresist pattern, comprising the steps of:
- (a) coating a photoresist composition of claim 11 on a substrate of a semiconductor element to form a photoresist film;
  - (b) exposing the photoresist film;
  - 5 (c) performing silylation process on the surface of the exposed photoresist film; and
  - (d) dry etching the photoresist film using the silylated layer as an etching mask to obtain a negative pattern.
- 10 18. The process according to claim 17 further comprising pre-treating the substrate with hexamethyldisilazane before performing said step (a).
19. The process according to claim 17 further comprising a baking step before and/or after the exposure step (b).
- 15 20. The process according to claim 19, wherein the baking step or steps are performed at the temperature ranging from 10 to 200 °C.
21. The process according to claim 17, wherein the exposing step is
- 20 performed employing ArF, KrF, EUV (Extreme Ultra Violet), VUV (Vacuum Ultra Violet), E-beam, X-ray or ion beam.
22. The process according to claim 17, wherein the exposing step is performed with an irradiation energy in the range of from 1 to 50mJ/cm<sup>2</sup>.
- 25 23. The process according to claim 17, wherein the silylating agent used in

silylation process is selected from the group consisting of hexamethyldisilazane, tetramethyldisilazane and bisdimethylamino dimethylsilane, bisdimethylamino methylsilane, dimethylsilyl dimethylamine, dimethylsilyl diethylamine, trimethylsilyl dimethylamine, trimethylsilyl diethylamine and dimethylamino pentamethyldisilane.

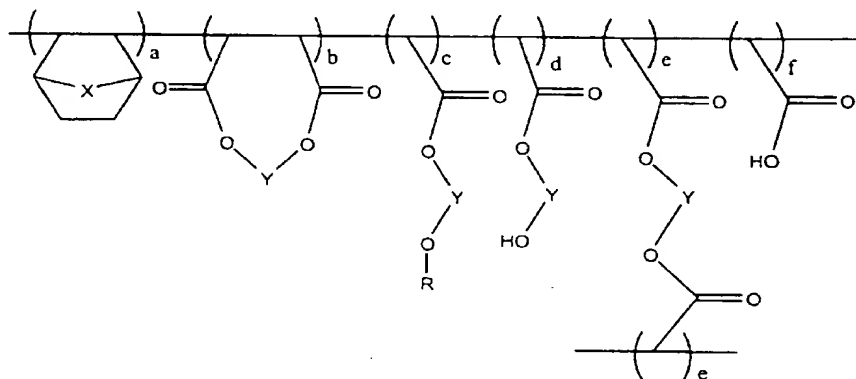
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24. A semiconductor element manufactured with the process of claim 17.

## ABSTRACT

The present invention relates to a photoresist polymer for a top-surface imaging process, and a photoresist composition containing the same. The protecting group of the photoresist polymer represented by Formula 1 is selectively deprotected in an exposed region, and thus a hydroxyl group is generated. The hydroxyl group reacts with the silylation agent to cause a silylation process. Accordingly, when the photoresist film is dry-developed, the exposed region only remains to form a negative pattern. In addition, the present photoresist composition has excellent adhesiveness to a substrate, thus preventing a pattern collapse in forming a minute pattern. As a result, the present photoresist composition is suitable for a lithography process using light sources such as ArF (193nm), VUV (157nm) and EUV (13nm).

[Formula 1]



wherein, X, Y and R are defined in accordance with the specification.